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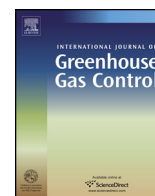
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Odourisation of CO₂ pipelines in the UK: Historical and current impacts of smell during gas transport



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ABSTRACT

Commercial scale Carbon Capture and Storage (CCS) will require CO₂ to be transported from industrial point sources to storage sites, potentially over distances of hundreds of kilometres. One of the most efficient means of transporting fluids over large distances is via pipeline. Pipeline leaks can be problematic, especially when transporting colourless and odourless gases such as natural gas and CO₂. One of the current methods of risk mitigation for natural gas transport is odourisation. The aim of this study is to determine why odourising has been suggested for CO₂ pipeline transport and what benefit it would add. This article reviews the history of gas odourisation during pipeline transportation. It also discusses the existing practices with respect to odourant use for CO₂ and natural gas transport in pipelines. Based on experience from natural gas, it is concluded that high pressure pipelines of CO₂ through sparsely populated areas could have odourant added, but will gain little safety benefit. However, adding odourant to CO₂ gas phase pipes could aid detection of leaks as well as improve public assurance and should be considered in more detail.

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1. Introduction

The capture and long term storage of CO₂ in the subsurface is one of the most favourable ways of mitigating the current level of CO₂ being released from large power and industrial point sources (Edenhofer et al., 2014; Haszeldine, 2009). The proven ability to transport CO₂ safely is an important requirement for the success of Carbon Capture and Storage (CCS) technology. Pipelines have shown to be the most important part of a CCS network to the public (Wallquist et al., 2012). Development of pipeline systems can be hindered in certain areas if there is no clear incentive between the benefits gained and how safe pipelines are perceived to be (Wallquist et al., 2012). There is existing literature for assessing individual and societal risk associated with natural gas and CO₂ pipelines (Cleaver and Hopkins, 2012; Knoope et al., 2014; Koers et al., 2010). With work focusing on existing approaches used for natural gas systems (Cleaver and Hopkins, 2012), it is clear that when different phases of CO₂ are involved the risk levels change (Knoope et al., 2014). Ensuring the low individual risks of 10^{−6}, (the likelihood per annum that a person at a fixed location is fatally injured) is more complicated for CO₂ transport than for natural gas, since CO₂ can be transported in a gaseous or dense phase. However, public perception is very important when addressing risk issues for pipelines (Jo and Crowl, 2008).

Pure CO₂ is colourless and virtually odourless. The artificial addition of impurities that enable olfactory detection ('odourising') could provide an additional attribute of safety in the event of unplanned CO₂ leakage, reducing the level of risk involved. Odourising CO₂ during pipeline transport has been suggested in relation to CCS (Barrie et al., 2004; Gale and Davison, 2004); to date only limited research has been undertaken into how effective or necessary it will be. The aim of this paper is to explore why odourising has been suggested for CO₂ pipeline transport and whether it would be worthwhile.

Here we investigate the implications of odourising CO₂ in pipelines for CCS and CO₂ Enhanced Oil Recovery (CO₂-EOR). We first review the social history of gas pipelines, in particular how odourising agents in gas have influenced public perception of natural gas transport. Then, we discuss the existing practices of natural gas transport and CO₂ in pipelines, with particular emphasis on the United Kingdom and North America. Finally, we consider the implications of odourant for transport of CO₂ in the United Kingdom.

2. Odourising natural gas

An odour is the property of a substance that gives it a characteristic scent or smell. The choice of odourant relies on the physical and chemical properties of the mixture. A suitable odourant for detection purposes should be able to permeate through soil but not through intact pipeline material. The odourant also needs to be

nontoxic but strong enough for a sensible recognition threshold; in short it should have a low threshold (perceived by human sense of smell) and with maximum impact.

2.1. History of odourisation

R. Von Quaglio first proposed odourisation of gas in Germany during the 1880's (Amirbekyan, 2013; Tenkrat et al., 2010). Efforts were made to add an odour to blue water gas (an industrial gas developed by Sir William Siemens, similar to town gas, composed almost entirely of carbon monoxide and hydrogen) using nitrobenzene and ethanethiol. By 1918, Germany began small-scale odourisation, with the United States of America doing so shortly after (Amirbekyan, 2013). The rise of automobiles and the onset of the Second World War led to many new chemicals and technologies for odourising being developed (Amirbekyan, 2013).

2.2. North America

Odourisation was initially performed on a voluntary basis in North America, with no government regulations to enforce it. In some areas of the continent, where 'gasoline' or butane was refined, untreated residue gases were gathered and returned to the lines either to be used as a boiler fuel or flared off. While it was not overtly approved, many public facilities in these particular areas obtained their gas directly from these low pressure residue lines, with no odourisation.

2.2.1. New London school gas explosion

On 18th March 1937, a natural gas explosion at the New London School in Texas killed 298 people (May, 2010); this would become a significant event to introduce mandatory odourising of gas. Earlier that year, the school board cancelled their natural gas contract and had plumbers install a tap into Parade Gasoline Company's residue gas line. The odourless gas had been leaking from the residue line tap, and built up inside an enclosed crawlspace that ran the entire length of the building. Shortly after 3.00pm, the instructor for manual training turned on an electric sander in a room with a mixture of air and non-odourised gas. The electric switch ignited the gas in the room and caused an explosion, which led to the destruction of the entire building.

An investigation by the United States Bureau of Mines following the disaster discovered the faulty connection to the gas line. On 28th May 1937, the State Board of Registration for Professional Engineers was created by the 45th Texas Legislature (Texas State Library and Archives Commission, 2006). Within weeks of this incident, the Texas Legislature mandated the addition of thiols (commonly referred to as mercaptans) to natural gas. This procedure then became worldwide; a major turning point for natural gas transportation procedures.

2.3. The United Kingdom

2.3.1. Coal gas

Coal gas (historically referred to as town gas) was first used in a practical application in 1792 (Gledhill, 2008) to heat the personal home of William Murdoch in Redruth, Cornwall. The first process used to form coal gas was destructive distillation: the liberation of gas by decomposing coal using high temperatures. Depending on the source of coal used and the level of refinement, the final product contains a variety of gases, primarily hydrogen (~49%), methane, CO₂ and carbon monoxide, as well as volatile hydrocarbons. Coal gas was dominantly used until the 1960's, when it was replaced by other forms of natural gas. Coal gas has a naturally distinctive smell associated with it, the result of an organic sulfur compound known as thiophene (a heterocyclic compound, C₄H₄S). This distinct sweet smell acted as an automatic safety device during the 1800's in the United Kingdom, which was important as some town gas (such as at the Poole Plant, Dorset) could have up to 15% carbon monoxide in it. Carbon monoxide is an extremely poisonous gas (resulting in damage to health) with a 0.0025% threshold, which can prove fatal above concentrations of 0.08% (EPA, 2013; Sonley, 2012).

2.3.2. Reformed gas

Technical advances improved the efficiency of gas manufacture. From the late 1950's, various high temperature reforming processes were utilised to make gas from petroleum products such as naphtha or propane; this reformed gas (gas produced from oil) had no discernible odour associated with it (Sonley, 2012). In keeping with the regulations as outlined by the Gas Acts during that time, a method of detection was necessary. At the time, operations were controlled by twelve area Gas Boards, which were governed by the Gas Council. Discussions took place to add a smell, which would be suitable and meet the Gas Acts requirements. Based on the odourants used in America, thiolane (THT, (CH₂)₄S) a saturated analogue of thiophene was selected (Sonley, 2012). Additionally, many of the coal gas pipes were reused which retained the distinct coal gas odour. This meant the reformed gas also retained the familiar warning smell the public were accustomed to for a limited amount of time.

2.3.3. Natural gas

Reformed gas was the dominant gas source for less than a decade. By 1959, the first liquefied natural gas was imported into Britain from the Gulf of Mexico. By 1965, natural gas was discovered in the West Sole field in the North Sea (Bamberg, 2000). In 1967, the natural gas conversion process commenced in Britain, which took up to ten years to complete (Arapostathis, 2011). As part of the conversion to North Sea natural gas, many of the original cast iron gas pipes installed in towns and cities for town gas were replaced with plastic pipes. It was also necessary to adapt or replace gas appliances around the United Kingdom, as the chemical makeup of the natural gas produced from the North Sea was overwhelmingly methane, different from the manufactured gas (Arapostathis, 2011). Natural gas from the North Sea is mostly odour free, although gas from some fields contains sulfur compounds giving the gas a 'rotten egg' odour. Initially THT was used in pipelines just as it had been for reformed gas (Sonley, 2012). Odourisation plants injected natural gas dosed up with 5 ppm THT in newly replaced high pressure transmission pipes, which transported gas at 6 MPa (Sonley, 2012). However, it was observed that samples of gas further down the line had lost the THT odour and in other cases, the gas had retained only some of the chemical components and developed a different smell. For example, in the Poole area during this period, the Customer Service Department for the local gasworks responded to a call where a woman had a strong smell of beetroot in her house. Upon investigation, the smell was due to a significant gas leak adjacent to her home (Sonley, 2012). Thus, the odourisation system

had 'worked' in the local distribution network, but was imperfectly understood.

2.4. Current natural gas pipelines

Natural gas pipeline systems are complex and their development has been influenced by other uncertainties – particularly those associated with political, regulatory and economic regimes (Arapostathis, 2011). The natural gas network is made up of a variety of pipelines, which have different conditions and purposes. A transmission line refers to a pipeline that transports gas from a gathering line (connection from a storage facility to a distribution centre, another storage facility, or large volume customer such as a power plant). It is normally maintained at high pressure. A transmission pipeline may carry gas at 11 m s⁻¹ across long distances and geographical boundaries (CEPA, 2015). A distribution pipeline refers to a lower pressure system, which delivers gas to end consumers via local service pipelines, and to appliances.

2.4.1. North America

Today in the United States of America, the odourisation of transported gas is regulated under federal legislation (US Government, 2012). All combustible gases transported in distribution lines are required to contain a natural or added odour that is readily detectable by a person with a 'normal' sense of smell. North American regulations require that natural gas distributed to end consumers must be detected at 1/5th of its lower explosive limit; this equates to 5% natural gas in air (US Government, 2012). Therefore, a fit individual with a normal sense of smell must be able to detect odourised natural gas at a concentration of 1% in air (Ivanov et al., 2009); the same requirement applies to the United Kingdom. Odourising of natural gas within transmission pipelines is not normally required unless they are in close proximity to households (US Government, 2012). Records show 2,059 accidents causing 106 fatalities and 382 injuries related to natural gas (and hazardous gas) pipelines occurred from 2002 to 2008 in the United States of America (Parfomak and Folger, 2009). Odourisation of low pressure pipes has been part of a great safety improvement in natural gas transport since 1937.

2.4.2. The United Kingdom

Over time and with research, alternative odour mixtures have been developed. Modern day natural gas in the United Kingdom is odourised in only the lower pressure distribution pipelines using an odour blend referred to as NB (New Blend). NB is a mixture of 80% 2-Methylpropane-2-thiol (TBM, (CH₃)₃CSH) with 20% methylthiomethane (DMS, (CH₃)₂S) (National Grid, 2006). The mixture of the two compounds performs well for detection of natural gas leaks (a mixture of rotten eggs with a cabbage-like smell). This type of mixture can have an odour threshold (lowest concentration detectable by sense of smell) as low as 0.1 ppb (Tenkrat et al., 2010). Today the National Transmission System (NTS) is a large network of gas pipelines (over 7600 km) which operates in the United Kingdom; it is owned and maintained by National Grid plc. These high pressure pipelines are not odourised and as gas leaves this transmission network, it is odourised for natural gas supplies that flow through local distribution systems at 6 mg sm⁻¹ (Marcogaz, 2006, 2012; National Grid, 2014). The eight lower pressure distribution networks for domestic use are maintained for end consumers by local gas transporters and third party independent systems. Deaths from gas pipelines have continued to fall because of progressive replacement of iron mains pipes; in 1990–2012, there were 1.4 fatalities per year, since 2002, just 0.4 per year (Health and Safety Executive, 2012/13).

3. Odour fade in pipelines

Here we define odour fade as the gradual reduction of a distinctive smell. The reduction in the performance of an odourant in transported gas is not a new problem (Usher, 1999). The causes of odour fade may be the result of odour fatigue; however, in some cases it can be the result of olfactory adaptation by people. For the purpose of this paper, odour fade refers to reduction in the efficiency of an odourant gas itself. This is an operational issue, as opposed to olfactory adaption whereby an individual loses the ability to distinguish a particular odour after prolonged exposure to it. In most cases, this is a temporary loss of ability, but can prove to be a degenerative issue too (Stevens et al., 1987). Odour fade can be a major issue, if odourisation is the primary means of detection. This section of the paper will focus on the reduction of efficiency in transmitting smell due to odour fade.

3.1. Causes of odour fade

Odour fade occurs when the odourant added to gas within the pipe are reduced because of physical and chemical processes (Usher, 1999). These are important processes to consider when identifying potential issues. The processes involved are:

3.1.1. Adsorption

Odourant molecules adhere to the interior of the steel pipe. During adsorption, the odourant creates a film on the surface of the pipe. Adsorption is a consequence of surface energy; the pipe surface is not wholly surrounded by other atoms and as a result can attract adsorbates, i.e. the odourant. During adsorption, the nature of the bonding depends on the involved species. Adsorption can be divided into *physisorption*, which is governed by weak van der Waals forces; and *chemisorption*, which involves covalent bonding. The level of odourant lost to adsorption is calibrated by isotherms (a curve giving the functional relationship between adsorbate and adsorbent in a constant-temperature adsorption process). The amount of odourant lost on the surface of a pipe is a function of its pressure (for a gas) or concentration (for a liquid) at constant temperature.

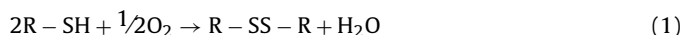
3.1.2. Absorption

Odourant molecules dissolve into, or combine with, the pipeline material. Absorption involves the whole volume of the bulk material. Until sorption equilibrium is reached, the odour concentration will continue to reduce. Absorption is a combined physical and chemical process. Physical absorption occurs between a gas mixture and liquid solvent. Chemical absorption is a reactive process. The nature of absorption of an odourant is dependent on the stoichiometry of the system as well as the odourant concentration.

It is important to note that as well as sorption processes, desorption may also occur. This is exemplified by the intentional odourisation of reformed gas in the United Kingdom during the 1950's, in pipelines which previously transported naturally odourised town gas.

3.1.3. Oxidation

This occurs when iron oxide or other compounds react with the odourant to change its chemical composition. Oxidation is the loss of electrons; although it may also be an increase in oxidation state (the actual transfer of electrons may never occur). Oxidation of thiols to disulfides may be represented by the following equation (such a reaction is faster if supplied with FeO_2):



Oxidation is more common in new steel pipes than plastic or old steel pipes. When a new natural gas steel pipe is installed, the

inner walls are porous and contain metal oxides such as rust and mill scale (flaky surface of hot rolled steel, iron oxides consisting of Fe (II) and Fe (III) oxides, hematite and magnetite). Metal oxides are very reactive with odourants and can produce disulfides, which are less odourous than the original mix (e.g. TBM).

3.2. Remediation of odour fade

To overcome the issue of the odour fade in gas pipelines, it is necessary to perform a process known as 'pickling' to a pipeline. Every pickling regime is different depending on the length and diameter of the pipe, the material involved and the type of gas to be transported. However, there are three basic methods that can be used to for pickling and gas pipeline pre-odourisation. These are:

- 1) The injection of highly odourised gas (40 ppm).
- 2) Slugging: this involves the injection of a bulk amount of odourant into a defined and isolated length of pipe.
- 3) Continuous injection of a controlled volume of liquid odourant into the gas stream flowing through the pipe (Ivanov et al., 2009).

Even after over-odourising the gas pipeline through the pickling process, odour fade can start again after a few months and the process may need to be repeated. In addition to any odour interaction with pipeline materials, any released odourant in a gas leak will be affected by contact with soils. Soils with high clay content tend to remove and retain odour more effectively than sandy soil. Soils with high iron or metal content will react with the odourant to reduce its olfactory strength.

4. Odourising CO_2

The quantity of odourant required for odourising a CO_2 pipeline will depend on a number of factors. Currently the common amount of odourant added to a low pressure natural gas pipeline ranges from 2–4 ppmV (by volume, by gas) (Max Machinery Inc., 2015). This amount is well above the minimum detection threshold of most commonly used odourants. In the event of a breach, it must account for many possibilities, including but not limited to clear recognition, odour fade, soil penetration and dispersion rate from the pipe.

There are no existing recommendations for odourising CO_2 pipelines. If odourants are to be used to assist monitoring leakage of CO_2 then it could be apt to follow the procedures initially and recommendations used when transporting natural gas in pipelines. However, the addition of odorant should be based on the toxicity of CO_2 rather than lower explosive limit (as CO_2 is not flammable). The actual volume of odourants added depends on the potency of the mixture chosen, the flow rates/velocity of the fluid, baseload capacity of the capture station, the phase of the fluid and the purity/quality of the fluid being transported. Difficulty may also arise where two-phase flow may occur along the pipeline system.

4.1. Impurities in CO_2

CO_2 transport is complicated by the presence of impurities within the transported CO_2 . How much of each impurity is present depends on the source reservoir geochemistry or the type of capture technology if it is from an anthropogenic process (Allis et al., 2001; IEAGHG, 2011). Common contaminants can be nitrogen, oxygen, argon and moisture (IEAGHG, 2004). None of the capture methods (pre-combustion, post-combustion, oxyfuel) seem to produce any thiols during the process (IEAGHG, 2011). However, there can be traces of hydrogen sulfide and other sulfur compounds that could lead to an unintentional odourising effect.

Table 1
Existing long distance CO₂ pipelines within North America (Gale and Davison, 2004).

Pipeline	Location	Origin of CO ₂	Capacity (Mt CO ₂ yr ⁻¹)	Length (km)
Cortez	USA	McElmo dome	19.3	808
Sheep mountain	USA	Sheep mountain	9.5	660
Bravo	USA	Bravo dome	7.2	350
Canyon reef carriers	USA	Gasification plants	5.2	225
Val Verde	USA	Val Verde gas plants	2.5	130
Weyburn	USA and Canada	Gasification plant	5.0	330

These impurities may require treatment prior to transportation. Impurities influence the hydraulic parameters such as the pressure and temperature conditions, but also the density and viscosity of the fluid, depending on what impurities are present. For example, the presence of hydrogen or nitrogen can produce larger pressures and temperature drops in transported CO₂ (Health and Safety Laboratory, 2009). Excessive water content in CO₂ can cause formation of highly corrosive carbonic acid, which can corrode and alter the integrity of the pipelines (Heggum et al., 2005; Li et al., 2011). While the solubility of water in pure CO₂ is well known as a function of pressure and temperature, few data are available for the effect of trace chemicals on solubility. Use of carbon steel pipelines for CO₂ transport will require that the CO₂ is dried to eliminate any free water. Moisture in the gas should be removed prior to transportation or inhibitors should be used to reduce corrosion caused by the free water. Carbonic acid can lead to corrosion rates of up to 1–2 mm within two weeks on standard carbon steel pipelines (Seiersten, 2001). A drop in pressure would result in two-phase flow leading to some gaseous phase being formed; compressor stations between fixed distances would reduce this. The distance between the stations would depend on many variables of the system including initial temperature and pressure, the conditions of travel and the chemical composition of the fluid (IEAGHG, 2004).

4.2. CO₂ pipeline experience in North America

Approximately 6000 km of CO₂ pipelines are in operation in North America (Amann, 2010) and these have experienced few serious accidents. Thirty-one leaks from CO₂ pipelines were reported from 2002 through 2008, none resulting in personal injuries (Parfomak and Folger, 2009). It is difficult to directly compare natural gas and CO₂ incidents, as the CO₂ pipeline network is only ~1% of the size of the natural gas network, i.e. about the length of the United Kingdom gas pipe network. In addition to this, the CO₂ pipelines primarily run through remote areas and are normally transporting CO₂ as a dense phase.

The oldest long distance CO₂ pipeline in the United States of America is the Canyon Reef Carriers Pipeline in Texas; it is 225 km in length and has been in use since the early 1970's (Table 1). Many other pipelines have been constructed since then and opened up the network for CO₂-EOR (Amann, 2010). The properties of CO₂ make it an especially effective solvent for EOR. The CO₂ transported in these pipelines are derived from a variety of sources: naturally occurring underground reservoirs, natural gas processing facilities, ammonia manufacturing plants, as well as coal gasification plants producing synfuel. Currently, most of the CO₂ for EOR is sourced from natural CO₂ reservoirs and synfuel. However, as CCS gradually develops, the use of anthropogenic sources for EOR would provide a demand for CO₂ and require additional transport infrastructure to make it feasible. In the United States of America, CO₂ pipelines are subject to diverse local, state and federal regulatory oversight (Serpa et al., 2011). Currently, there is no evidence that CO₂ pipelines in North America are being intentionally odourised during CO₂ transport; nor are they legally obliged to do so.

4.2.1. North America - high pressure pipeline transport to onshore storage site

The Great Plains Synfuels Plant, Beulah, North Dakota, United States of America (owned by Dakota Gasification Company) provides anthropogenic CO₂ to the Weyburn oilfield for EOR. The Great Plains Synfuels Plant receives crushed lignite from the nearby Freedom Mine (The North American Coal Corporation, 2006). The lignite contains 37% water, has an ash content of 7.5% and a sulfur content of 0.8% (Riding and Rochelle, 2005). The normal feedstock for the gasification plant is lignite but the Dakota Gasification company also occasionally use waste, biomass and car tyres. This could lead to a variation in the composition of the synthetic fuels and products produced. The produced CO₂ contains several different kinds of thiols as well as H₂S (Table 2). Dakota Gasification Company does not add any additional odourant. The mined lignite does not appear to have any properties that make it unique compared to other lignite feedstock. Thiols can account for a percentage of the natural sulfur content in lignite (Elsevier IEA, 2013). The gasification process used to produce the CO₂ (Perry and Eliason, 2004) also has the ability to contribute to the level of thiols found in the CO₂ formed.

The produced CO₂ is transported via a 330 km long, carbon steel pipe (Riding and Rochelle, 2005). Three compressors are used to increase the pressure of the CO₂ to a very high pressure of about 15.2 MPa to maintain the transport as a dense fluid through the pipeline. The pipeline is 14 inch (355 mm) diameter from the Dakota Gasification Company Plant to the Tioga junction in North Dakota and is 12 inch (305 mm) the rest of the way to Weyburn. Early in the EOR operations, the removal of thiols was investigated to reduce the odours from operational CO₂ release in the area of the injection wellheads, but ultimately it was decided that it would have been too expensive for the benefit gained (Riding and Rochelle, 2005). Instead, all CO₂ injection wells are enclosed within housing facilities to reduce the emission of thiols to the public in the area of the EOR field (Perry and Eliason, 2004).

The Great Plains Synfuels Plant currently has a pipeline capacity designed for transporting around 6,500,000 sm³ d⁻¹ of CO₂. The CO₂ that they currently transport has a mole % of 0.03 of thiols (and other sulfides); this is 300 ppmV (~1,000 mg sm⁻³) and is substantially greater than the recommended 6 mg sm⁻³ amount currently added to United Kingdom natural gas pipelines. It is possible to consider this high pressure CO₂ pipeline as an example of a 'transmission pipeline' in the same manner as natural gas networks. This

Table 2
CO₂ gas composition from Dakota Gasification Company (updated 2008, average of >300 samples) (Dakota Gasification Company, 2008).

Parameter	Units	Typical result
CO ₂	Mol%	96
C2+ and hydrocarbons	Mol%	2
Hydrogen sulfide	Mol%	1
Nitrogen	Mol%	0.4
Methane	Mol%	0.9
Oxygen/argon	Mol%	<0.01
Thiols and other sulfides	Mol%	0.03
Moisture	ppmV	<20

Table 3

Pipeline maintenance carried out on high pressure CO₂ pipeline (Dakota Gasification Company, 2008).

Scheduled jobs	Annual frequency
Aerial patrols	26 times a year
Population density survey	Once every two years
Right of way inspection	26 times a year
Valve maintenance and inspection	Twice a year
Emergency systems check	Once per year
Rectifier maintenance	Six times a year
Cathodic protection survey (for external corrosion)	Once per year
Internal inspection of pipeline (electronic tool)	Every five years
Overpressure safety devices	Once per year
Public awareness and damage prevention programme	Once per year

suggests that coal gasification plants may produce thiols in the CO₂ and clearly shows that existing CO₂ high pressure pipeline infrastructure has the ability to transport large amount of thiols without any major detriment to the system (Miller and Pouliot, 2008). In addition to this, it suggests that any existing sulfur content in the CO₂ streams may produce enough smell without additional thiols added (this would be dependent on the capture method as well as the source of the CO₂). However, extensive technologies are already in place for monitoring along the pipeline. Dakota Gasification Company carries out a series of scheduled jobs that consist of preventive maintenance and patrols (Table 3). Since pipeline maintenance is already well established for the high pressure pipeline, added odourant might not be considered as necessary. In North America, few of the CO₂ transported in other existing pipelines from natural reservoirs contain detectable levels of sulfur compounds, with the exception of McElmo Dome, Colorado and Big Piney, Wyoming (Allis et al., 2001).

4.3. United Kingdom – low pressure pipeline transport to offshore storage site

There are no clear specifications for the composition of CO₂ transported within Europe, other than that the level of impurities present should not adversely affect the integrity of the storage site, transport system or be a risk to the surrounding environment/human health (EU Directive, 2009). The following information is based on the environmental statement which investigated the retrofitting of CCS technology to the Longannet Power Station, released by the Scottish Power Consortium (despite detailed investigations this demonstration failed to receive sufficient funding to go ahead) (ScottishPower CCS Consortium, 2011a). Research undertaken for the test pipelines provided potential design specifications for CO₂ transported from Longannet Power Station (Table 4); it also recommended that only minimal quantities (ppb) of carbon monoxide, hydrogen sulfide, methane or hydrocarbons should be permitted in a CO₂ pipeline.

Table 4

Provisional CO₂ design specification for transfer from onshore to offshore pipeline via compressor outlined by Scottish Power Consortium (ScottishPower CCS Consortium, 2011a).

Component	Units	Minimum	Maximum
CO ₂	Mole fraction	0.994	1
N ₂	Mole fraction	0	0.006
H ₂	Mole fraction	0	0.003
Ar	Mole fraction	0	0.006
O ₂	ppmV	0	1
H ₂ O	ppmW	0	50
Hg	ppb	0	<1
Particulates	microns	0	<7

The construction of an additional portion of pipeline (approximately 1.35 km) would be needed to connect the captured CO₂ from the Longannet Power Station (Fife, Scotland), to the existing 250 km reused natural gas pipeline to transport it to the St. Fergus Gas terminal (Peterhead, Aberdeenshire). Once at Peterhead, there is c. 100 km of offshore pipeline to reach the Goldeneye Platform. The odourisation of the transported CO₂ would only be required from the capture site to the terminal at Peterhead (once offshore the CO₂ would be pressurised and away from the general population). The CO₂ in the onshore portion of the pipeline would be transported as gas phase, well below the maximum operating pressure of the system; for this reason it is possible to consider this CO₂ pipeline as a 'distribution pipeline' in the same manner as natural gas systems. The addition of odourant in this case would be potentially valuable in public detection of minor leaks by smell.

5. Pipeline leaks

Different countries legislate for pipeline integrity monitoring in different ways (Stafford and Williams, 1996). Pipelines are subject to preventive maintenance as well as monitoring by a variety of methods (Dakota Gasification Company, 2008; Stafford and Williams, 1996). If sufficient damage is inflicted to a pipeline, the system will fail and loss of containment can incur. The cause of failure can be a number of individual factors or a combination such as – natural events, human factors, material defects and corrosion, and transport variables.

5.1. Health effects of natural gas and CO₂ leaks

Natural gas and CO₂ have very different chemical and physical properties. How they may affect the health of the public during exposure is determined by these properties. Natural gas has a very low density and is mainly composed of methane. In terms of public safety, this means that natural gas is an extremely flammable gas that can spread over long distances. CO₂ is denser than air but non-flammable, meaning it can 'pond' in sheltered locations at hazardous concentrations, and displace the normal oxygen concentration in the air. CO₂ is a poison which can cause hypercapnia (the incomplete exchange of gas in the lungs leading to increased concentration of CO₂ in the blood) (Roberts et al., 2011), and as a result unplanned release of CO₂ can lead to the poisoning and injury or death of animals or humans in that area, at concentrations above 5–10%. For CO₂ to reduce the oxygen concentration down to a level that is immediately dangerous to life, the CO₂ concentration would need to as high as 50% (Harper et al., 2011). Much work has been done to advise the amount and level of exposure of CO₂ to humans (Health and Safety Executive, 2011; Knoope et al., 2014); Table 5 summarises the main possible side effects of being exposed to both.

5.2. Natural gas leaks

With a natural gas pipeline leak, depending on the pressure, there will be an immediate and rapid depressurisation within the pipeline, followed by a relatively stable release of gas if pumping through the pipeline continues. Leak detection is heavily dependent on the leak size; safety monitoring sensors should activate in response to the pressure decrease and flow will be stopped once the necessary valves have been shut down (Stafford and Williams, 1996). Issues with a leakage from a high pressure natural gas pipeline include the explosive projection of pipeline material, a high level of noise as the gas is released and the possibility ignition of the initial gas in the form of a flare. If a release of gas does not ignite immediately, it will form a buoyant cloud less dense than air, which will disperse over large distances. If a cloud of gas ignites (once it has reached its lower explosive limit), it may burn back as a flash fire to the point of origin. The hazard range

Table 5
Effects of natural gas and different phases of CO₂.

Material	Description
Natural gas (methane + others)	Extremely flammable gas that will ignite – burns/death. Headaches, breathlessness from low level exposure. Flu-like symptoms from high level exposure. Prolonged exposure leads to loss of consciousness (/death).
CO ₂ (gas)	Adverse effects on the respiratory, cardiovascular and central nervous system due to increased acidity from low level exposure – hypercapnia symptoms (>3%). Increased respiration, confusion, unconsciousness, coma/death (>15%). High levels (>50%) immediately dangerous to life – but unclear whether death due to toxicological effects of CO ₂ or due to oxygen depletion.
CO ₂ (dense phase)	Rapid depressurising leads to poisoning from vapours emitted. Contact with skin causing cold burns.
CO ₂ (solid)	Sublimation to a vapour leads to poisoning. Loss of containment leading to the emission of high velocity solid particles.

for a pipeline release depends on the type of release as well the prevailing weather at the time of release.

5.3. CO₂ pipeline leaks

When the structural integrity of a pipeline is compromised, there is a chance of a failure. A pipeline failure is defined as an uncontrolled release of CO₂ and commonly known as a blowout. During a blowout, if supercritical CO₂ is being transported it will convert from the supercritical state to vapour phase as it expands. When the CO₂ is rapidly released, it will make a loud ‘hissing’ noise as the CO₂ cools and expands. This is known as the Joule-Thomson effect (Det Norske Veritas, 2010). This vapour is not flammable, but is denser than air, so can concentrate locally in hollows or low points of buildings, potentially leading to CO₂ poisoning. Once the CO₂ stream falls beneath the triple point temperature and pressure (216.55 K and 0.517 MPa) (Det Norske Veritas, 2010), solid dry ice particles can form. This cold CO₂ condenses water in the atmosphere, resulting in a white vapour cloud. It should be noted that there is some difficulty in modelling and therefore predicting the behaviour of CO₂ once it transitions from its dense phase to a gas phase upon depressurisation.

The solvent properties of pure supercritical CO₂ on its own can damage some elastomers commonly used in valves, gaskets, coatings and O-rings used for sealing purposes in pipelines (Mohitpour et al., 2008). Elastomers can be permeable to CO₂ and may allow the CO₂ to diffuse into the body of the material. Care must be taken when choosing a suitable material and re-using existing natural gas pipelines. This increases the susceptibility of a pressure release, which may cause explosive decompression and blistering. Some synthetic lubricants can harden in the presence of CO₂. However, experience from pipelines transporting CO₂ under constant pressurised conditions show no detrimental effects (Mohitpour et al., 2008). Problems arise when there is rapid decompression within a CO₂ pipeline. As the pressure outside the elastomer falls below that of the CO₂ contained in the elastomer, the CO₂ begins to expand and move towards the surface, which can lead to fractures or ruptures (Mohitpour et al., 2008).

Research has suggested that escaping gaseous CO₂ has a larger 10⁻⁶ location risk distance than dense phase CO₂ (Knoope et al., 2014). This is due to the dense phase being rapidly released as the CO₂ cools and expands to form a smaller but higher jet that has a higher mixing rate with the air than the gaseous CO₂ blanket (Knoope et al., 2014).

6. Discussion – odourisation for CO₂ pipelines

6.1. Discussion of historical evolution

This paper has described the past and current experiences with odourisation of natural gas and CO₂ transport networks. Engineer-

ing experience started with transport of coal town gas; initially these pipelines contained odour as part of the gas manufacture, and this proved to be a useful aid to detection of leaks from local, low pressure, pipeline networks. Compulsory odourisation was introduced into pipelines as an additional inherent safety measure of detection of an invisible, odourless, potentially hazardous gas that may have been unintentionally released. However, odourisation does require additional design and maintenance – the odourants need to be carefully chosen, injected and maintained. Odourants can fade, by sorption processes in pipes, especially with iron, steel, or rust; this may require regular interruption to normal services to impregnate pipes with odourant and minimise the fade of smell. Subsequently, the natural gas network in both the United Kingdom and North America has developed into a highly integrated system of transmission and distribution lines established to accommodate the demand for energy. In the United Kingdom and North America all distribution and service natural gas pipelines operate at a low pressure range and contain odourants for identifying an unintentional release. These lines enter populated areas, and the lowest pressures transmit odourised gas into domestic houses. In such cases, the addition of smell adds an important additional safety aspect, and smell detection by the public is clearly implicated in avoidance of many accidents. Consequently, there is a well-established and positive public perception of gas odour as a safety measure. Gas in high pressure, long distance, transmission pipelines is transported at a much higher pressure; these pipes run beyond heavily populated areas. Any gas leaks can be readily and rapidly detected by pressure drops, and so the gas is not routinely odourised.

6.2. Different purposes of natural gas and CO₂ pipelines

It is important to realise that the developmental reasons behind an odourised natural gas and CO₂ network are very different (Arapostathis, 2011). These differing origins, purposes and geographic extent of the pipe network, are expected to influence how society interacts with the operation of pipelines. Natural gas is an energy source, introduced pervasively throughout urban areas to replace the less efficient and less sustainable town gases. It is also buoyant and does not poison humans because it is dispersed rapidly – the main risk is explosive combustion. CCS is a technology designed for mitigating the current level of CO₂ being released from large industrial point sources. The intention is to gather CO₂ from industrial sites and aggregate this to shared-access regional transmission pipelines, which are intended to operate with dense phase CO₂ at high pressures (greater than 70 MPa). CO₂ is an odourless gas and can lead to poisoning if released and ponded, or to asphyxiation in high concentration. CCS, and its pipes, does not have a direct relationship with the population. CO₂ is not consumed in the same way as natural gas, and provides no direct benefits for

individual households. There is no need for physical transport of CO₂ from or to individual households. Nevertheless, as with the natural gas network, it would become more complex and closer to more densely populated regions as it developed. There is existing experience since 1972 in operating CO₂ pipelines in the United States of America and Canada. These are effectively single pipes, at high pressure, which flow under controlled conditions to feed CO₂ into CO₂-Enhanced Oil Recovery projects. These are currently not required to be odourised but do predominately pass through sparsely populated regions.

6.3. Development of a CCS network for the United Kingdom

In the existing scenarios for CCS, a CO₂ transport network would evolve from individual pipes, to more complex networks where additional sources of CO₂ are progressively tied-in to increase the throughput in a shared 'common-carrier' trunk pipeline (Stewart et al., 2014). These could be viewed as analogous to the local distribution and the long distance transmission pipes for natural gas. This evolution, and clustered gathering, is important because it could produce different approaches through time and space in monitoring and odourising of CO₂. For example, the published design for post-combustion CCS on the Longannet power plant in Scotland (ScottishPower CCS Consortium, 2011b), planned to re-use an existing natural gas transmission pipeline capable of operating at high pressure. It would be necessary to build a specific new link from the power plant, to link in to the transmission line. Even though route choice was careful, this was planned to be in a congested area (ScottishPower CCS Consortium, 2011b). So in that sense, this project is a vision of second or third generation of power plant, linking to an established transmission system. To obtain easier Health and Safety Executive clearance, and avoid public dissent, the link pipe was planned to be operated as a pressured CO₂ gas, analogous to local distribution in natural gas. A surprising feature of the design was that the quantity of CO₂ was small, at 2.5 Mt yr⁻¹, which was much smaller than the >10 MtCO₂ yr⁻¹ capacity of the high pressure pipe. This was likely due to design pressures along the system to avoid two phase flow (IEAGHG, 2013); the decision was taken to run the long distance transmission pipe at low pressures of 2.8–3.4 MPa (ScottishPower CCS Consortium, 2011b). Therefore, in this project, both pipeline types were to be run at low pressure and, even with a scaled up project, the local distribution pipe would transport the CO₂ as a gas at 3 MPa. Consequently, some of the arguments for enabling detection of small leaks by smell, which favoured adding odourant to low pressure natural gas pipelines, could apply. The mass of CO₂ running through a local CO₂ pipe, even at a low pressure, will be very large – at least 1 MtCO₂ yr⁻¹. In a long distance pipe, the inherent pressure drop along the route and the variability in operating pressure due to fluctuating CO₂ supply make it difficult to use small losses of pressure as a failsafe method for detecting leaks.

There are additional important differences between CO₂ transport and natural gas transport. Captured CO₂ from CCS will have a different chemistry which could contain up to 5% in a variety of impurities depending on the CO₂ source and capture technique used (IEAGHG, 2011; Serpa et al., 2011). A CCS pipeline will not have static flow due to the imbalance of supply from source to storage point. Intermittent transport can trap excess CO₂ with impurities, which can react with the pipeline materials. Existing North American pipelines used to transport CO₂ for EOR generally pass through remote, unpopulated onshore areas. Pipelines for the transport of CO₂ destined for storage would be significantly closer to populated areas in European countries, and in the United Kingdom, some will be offshore (Cosham and Eiber, 2008). This is an important factor to consider when deciding how best to monitor the pipelines for leakage.

Although CO₂ is not currently regulated as a dangerous fluid (Health and Safety Laboratory, 2009), under the Pipeline Safety Regulations 1996, Part II of those regulations defines the legal standards for pipeline design and operation (Parliament of the United Kingdom, 1996); other regulations also already exist to cover the transport of CO₂; the Health and Safety at Work etc. Act 1974 requires employers to manage risks from CO₂ at every stage along the pipeline (Parliament of the United Kingdom, 1974).

7. Conclusion

Existing technologies for monitoring are already well established for high pressure natural gas pipelines as well as for CO₂ pipelines without using odourisation as a detection method. However, public perception is very important when addressing risk issues for pipelines. As CO₂ pipeline networks are established into regions which are not familiar with CO₂ transport (i.e. outside of North America), then for public reassurance it may well be beneficial to odourise the gas phase, low pressure, CO₂ pipelines during the first projects developed. To date there are no clear specifications for the composition of CO₂ transported within Europe. In the United States of America, CO₂ pipelines endure diverse local, state and federal regulatory oversight. There are no direct specifications in place for odourisation of CO₂. For management of odourisation of CO₂ pipelines, further investigation is needed into the interaction of specific impurities associated with captured CO₂ on the odourants, the transport of different phases of CO₂ and the result of intermittent operations; the financial costs involved for effective implementation must also be considered.

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